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## The Thermal Efficiency of the Rotary Cement Kiln.\*

By HANS GYGI. (Zurich)

(Continued.)

III.—THE PROCESSES OF HEATING AND BURNING.

#### (1) Recording of Temperatures within the Kiln and the withdrawal of Samples of Material at various Cross-sections.

The heat balance provides data for the production of clinker per unit of time and for the consumption of coal. On the basis of the heat balance a reliable estimate of the efficiency of the kiln can be formed, because it shows what proportion of the heat input is usefully expended and what proportion is lost.

But it gives no information about the processes that go on inside the kiln, although it is of the greatest importance to possess sufficient knowledge of these processes to enable the heat losses to be restricted to a minimum in practice. To elucidate conditions within the kiln it is necessary to sample the material and to measure its temperature as well as the temperature of the gases at intervals along the kiln axis. This can be done by the sampling ports provided in the casing. Furthermore, it is important that the variation in the temperature of the inner surface of the lining during the rotation of the kiln should be determined for the various cross-sections.

#### Measurement of the Temperature of the Raw Material.

The pyrometer used to measure the temperature of the raw material is shown in Fig. 7. The insulated platinum/platinum-rhodium thermocouple is protected by a Freiberger tube which, in turn, is encased in a "Silit" tube. Actually the platinum/platinum-rhodium couple was only used for determining the high

Previous articles in this series appeared in our issues for November and December, 1937.

material temperatures at cross-sections 7 to 12. At cross-sections 1 to 7, a nickel/nickel-chromium thermocouple, which was placed in the Freiberger tube instead of the platinum/platinum-rhodium thermocouple, gave better results. The Freiberger tube is contained in a "Silit" tube which fits into a metal tube, the purpose of which is to protect the "Silit" tube from damage when the screws of the adjusting ring are tightened.

During the experiments, the kiln was stopped when necessary for fitting the pyrometers and started again as soon as possible afterwards. As soon as it could be assumed that the equilibrium condition had again been reached the kiln was stopped in such a position that the Freiberger tube was completely embedded in raw material. The ends of the thermocouple were then connected to the circuit which lead to the millivoltmeter and the reading was taken as

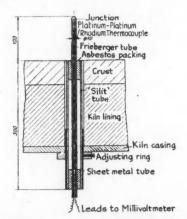


Fig. 7.—Pyrometer used for measuring the temperature of the material within the kiln.

soon as a steady voltage was recorded. At the same time the temperature of the cold junction was read and corrected and the value was added to the temperature reading from the instrument. In this manner the temperature of the material was determined for all cross-sections without any considerable difficulty; the results so obtained may be regarded as reliable.

#### Sampling the Material.

In connection with these temperature measurements, it was of special interest to determine the water and carbon dioxide contents of samples of the raw material and, for those taken from the hotter cross-sections of the kiln, the free-lime content as well.

Water content was determined by drying in a desiccator, carbon dioxide by the Fresenius-Classen method, and free lime by the Schläpfer-Bukowski method.

#### Temperature of the Material and Changes in its Composition during Heating.

The results obtained are given in Table 7, and in Fig. 8 are shown the changes in composition that take place during the heating of the quantity of raw material required to produce r kg. of clinker.

TABLE 7.—CARBON DIOXIDE, INSOLUBLE AND FREE LIME CONTENTS OF 14 SAMPLES OF MATERIAL TAKEN FROM THE KILN.

No. of sample	CO <sub>3</sub> (%)	Insoluble (%)	Free lime (%)
Slurry inlet	33.28	17.90	0.00
I	33.27	17.89	0.00
2	33.29	17.88	0.00
3	33.21	17.67	0.00
4	32.71	16.71	0.00
5	32.50	16.55	0.00
6	32.50	15.35	0.00
7	30-46	11.80	0.13
8	29.55	11-17	0.50
9	25.92	8.92	1.36
10	20.60	7.53	4.14
II	7.15	4.29	13.05
12	0.31	0.31	6.23
Cooler outlet	0.18	0.20	0.10

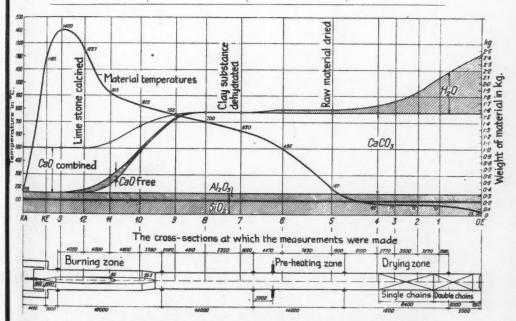


Fig. 8.—Changes in the composition of the raw materials required to produce I kg. of clinker, which occur during the process of burning in the klin, and the temperatures of the material at points along the length of the klin.

Consideration of the process of drying the slurry shows that most of the water is given up by evaporation at from 70 to 80 deg. C. About half way between cross-sections 4 and 5 the raw material is dry and the temperature now rises rapidly. In the vicinity of cross-section 6 the clay is converted into metakaolin and the water of crystallisation is expelled. The temperature curve for the material now gradually becomes flatter and between cross-sections 9 and 11, at temperatures from 750 to 900 deg. C., the carbon dioxide is driven off from the limestone. The greater part of the lime immediately combines with the silica and alumina, but there is distinctly a maximum free-lime content at cross-section 11. Between cross-sections 11 and 12 the temperature of the material mounts very rapidly; doubtless this is where the exothermic reactions commence which are associated with the formation of the cement compounds.

Unfortunately, there was no sampling port at the cross-section where the temperature of the material is at its highest and sintering is complete. It was therefore impossible to measure the sintering temperature directly and it had to be interpolated between the values recorded at cross-section 12 and the entrance to the cooler. The temperature so obtained was 1,400 deg. C.

#### Measurement of Gas Temperatures.

It is well known that the measurement of gas temperatures in industrial kilns is difficult, because thermocouples only give accurate values for gases when the walls by which they are enclosed have the same temperature as the gas. If the gas temperature differs from that of the wall the thermocouple does not measure the correct gas temperature but a temperature lying between that of the gas and that of the wall with which it is enclosed. The error increases absolutely and relatively with increase in temperature and also with increase in the difference between the temperature of the gas and that of the wall. The reason for this is that the thermocouple not only receives heat from the gas but also by radiation from the wall.

In view of the conditions obtaining in the cement kiln there could be no doubt that reliable readings of the gas temperatures could only be taken with a special pyrometer. The instrument used in these experiments was supplied by Messrs. Siemens and Halske. The nickel-nickel/chromium thermocouple is encased in an inner protective tube of "Nichrotherm." This tube is enclosed in another outer tube, also of "Nichrotherm," which is connected to the compressed-air pump. Between the inner and the outer tubes, at the level of the hot junction, there is a collar of ceramic ware furnished with numerous perforations, parallel to the axis of the tube, through which the gas flows at high velocity. M. Wenze and E. Schulze<sup>11</sup> have shown by thorough tests that it is possible to measure gas temperatures in industrial kilns with a pyrometer of this type with an error of less than 5 deg. C. The instrument is illustrated in Fig. 9, which also shows how it was fitted to the kiln.

When running normally, the kiln makes one complete revolution every 78 seconds, and at first it was found difficult to maintain the connection between the thermocouple and the millivoltmeter and to keep up a constant supply of

compressed air to the pump. Fig. To shows the arrangement finally adopted. The assistants on the service platform changed the connections to the compensating extension and the air pump as quickly as possible. The operation usually took 4 to 6 seconds.

The temperatures were measured on concentric circles in each cross-section. The first reading was taken at the kiln axis and others on circles having radii of 200, 400, and 600 mm. Readings could not be taken at greater distances from the axis, as there would have been a serious risk of the end of the pyrometer tube becoming embedded in the raw material during the rotation of the kiln.

The temperatures recorded are given in Fig. II together with the mean for each cross-section.

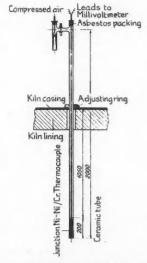


Fig. 9.—Pyrometer used to measure gas temperatures.

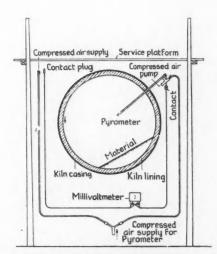


Fig. 10.—Diagram showing arrangement of apparatus for measuring gas temperatures during operation of the kiln.

The temperatures recorded when the pump was not in operation were always 120 to 150 deg. C. lower than the true gas temperatures. This observation could be made at every reading as the pump was not started until the values recorded by the millivoltmeter ceased to rise, which was usually after the kiln had made four or five revolutions. When this maximum was observed gas was drawn through the pyrometer tube and the instrument indicated a constant temperature again as soon as the kiln had completed one more revolution. The pyrometer was dismantled after each reading to ensure that the perforations in the ceramic collar were not choked. Usually they were open, but whenever more than 10 per cent. of the holes were stopped the experiment was repeated.

It was, unfortunately, impossible to obtain reliable values for the gas temperature at cross-sections 1, 2, and 3 with this instrument, because the pyrometer tube occasionally came into contact with the chains which were laden with moist raw material.

Neither was it possible to use the instrument to measure the gas temperatures at cross-sections 10, 11, and 12 in the burning zone, as the temperatures here were much too high. It is conceivable that readings could have been taken by means of a water-cooled pyrometer of this type, similar, perhaps, to the instrument used by Kühn<sup>12</sup> for his measurements of the gas temperatures in the combustion chamber of a boiler fired with pulverised coal. Nevertheless, a platinum/

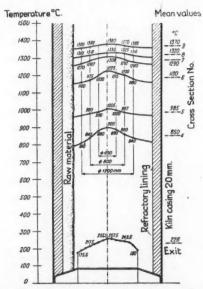


Fig. 11.—Gas temperatures measured at top end of kiln and at cross-sections Nos. 4 to 9.

platinum-rhodium thermocouple would not have sufficed for flame temperatures exceeding 1,800 deg. C. and it would have been necessary to use an iridium/iridium-rhodium thermocouple with protective tube and collar of especially heat-resistant materials. Furthermore, sampling ports of at least 120 mm. diameter would have had to be made in the kiln tube in the sintering zone, and it is doubtful whether this could have been done without destroying the refractory lining of the kiln near the ports. As other experimental difficulties were also to be expected it was thought advisable to refrain from making the attempt to measure flame temperatures. This occasioned but little embarrassment because it was possible to calculate the mean flame temperature for the cross-sections in the sintering zone.

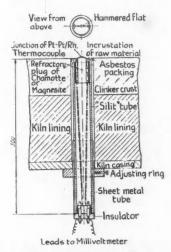


Fig. 12.—Pyrometer used to measure surface temperature of kiln lining.

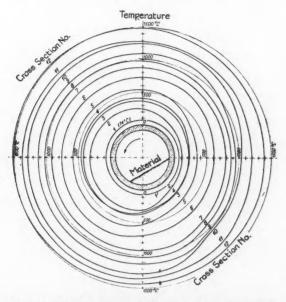


Fig. 13.—Temperatures of the inner surface of the lining at cross-sections Nos. 2 to 12 during one revolution of the kiln.

emperature °C.

## Measurement of the Temperatures at the Inner Surface of the Kiln Lining during a Revolution of the Kiln.

The pyrometer used for the measurement of surface temperatures is shown in Fig. 12, which also shows how it was fitted to the kiln. As the surface temperatures are subject to continuous variation during the rotation of the kiln, it was essential so to design the thermocouple that the hot junction responded to the variations in the surface temperature of the lining with as small a lag as possible. For this reason the thermocouple had to be of thin uncovered wire. In order that it should be sufficiently resistant to chemical attack, 0.5-mm. platinum/platinum-rhodium wires were used and the hot junction was hammered flat. Special attention was paid to the insulation of the two arms of the couple in order that no heat should be conducted away from the junction.

The same service platform was used for these experiments as for the measurement of gas temperatures. The connection between the thermocouple and the

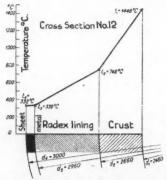


Fig. 14.—Temperature gradient through crust lining and kiln wall at cross-section No. 12.

compensating extension and millivoltmeter was again made by means of a plug and socket. Readings were made every five seconds and as each experiment comprised five revolutions of the kiln there were 78 readings to each run. In Fig. 13 are shown the temperature curves for the cross-sections I to 12 plotted from the results for five revolutions. For all cross-sections, except No. I where the surface temperature remained constant, the curves have the same characteristic shape.

The distribution of surface temperatures during a revolution of the kiln is of great practical significance for it shows that by increasing the speed of the kiln the maximum and minimum temperatures can be brought closer together. This results in more intensive heat transfer, and, what is more, the lowering of the maximum temperatures reduces the wear and tear of the lining in the sintering zone. It must, however, be borne in mind that it can only be

advantageous to increase the speed of the kiln if the inclination of its axis to the horizontal be reduced at the same time, otherwise the exposed surface of the material to be burned will be reduced to the consequent disadvantage of the heat transfer; and there will also be the risk that the raw material will pass through the sintering zone too quickly.

It was possible to carry out the measurements successfully in all cross-sections of the kiln without the hot junction becoming encrusted with material. In the

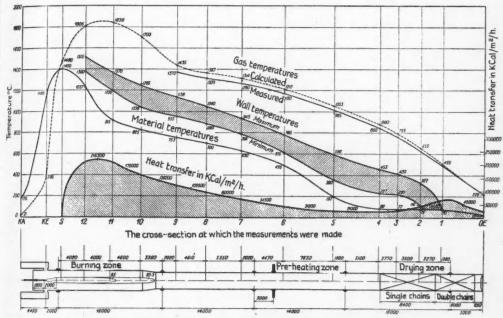


Fig. 15.—Gas temperatures, material temperatures, maximum and minimum temperatures at inner surface of lining and heat transfer in the kiln.

exceptional cases when this did happen it was immediately obvious from the temperature readings, and the experiment was repeated.

Temperatures in the interior of a rotary kiln were measured for the first time in 1921 by Professor Nacken<sup>14</sup> who used a similar instrument. But in this instrument there was a considerable loss of heat from the thermo-junction and the values obtained were too low. As the values obtained in the present experiment are the temperatures at the surface of the clinker coating on the lining, the temperature gradient across the composite wall—coating, lining, and casing—has been calculated and is shown in Fig. 14. The figure clearly shows the heat-insulating effect of the coating and demonstrates that the refractoriness of the lining is only necessary until the normal clinker coating has been formed.

#### Summary.

The values determined for the temperatures in the kiln have been assembled in the diagram shown in  $Fig.\,15$ , which shows the relationships of the gas, material, and wall temperatures to one another along the length of the kiln. It will be seen that the difference in temperature between gas and material in the drying zone is about 500 deg. C., and that this difference increases to about 750 deg. C. in the pre-heating, calcining, and sintering zones. The maximum wall temperature attained during one revolution of the kiln is about half-way between the gas and material temperatures throughout the kiln, while the minimum wall temperature is from 150 to 200 deg. C. below the maximum.

If it could be shown that there is a definite relationship between the measured gas temperatures and the measured material temperatures, the results obtained in this experiment would certainly have enhanced importance. The gas temperatures calculated for the various cross-sections of the kiln, which are also plotted in  $Fig.\ 15$ , confirm the existence of this relationship. The gas temperatures were calculated in the following manner.

The clinker production and the volume of exit gas are known from the output data and the heat balance of the kiln so that, by taking into account the temperature and the chemical composition of the raw materials, it is possible to calculate the volume of gas at any given cross-section. Furthermore, the amount of heat required to bring about a given increase in the temperature of the raw material can be calculated from the specific heats and the heat effects. Finally, the radiation losses are known for each cross-section of the kiln. By calculating the amount of heat required to bring the material at the temperature measured at cross-section 1 to the temperature measured at cross-section 2, and adding the radiation losses for this length of the kiln, we obtain the increase in the heat content of the gases between the two cross-sections. As the volume of gas and its heat content are now known for both cross-sections, the gas temperature can be calculated for these, and in the same manner for any other cross-section of the kiln.

The calculated gas temperatures are shown in Fig. 15; they are in every case higher than the measured temperatures. As the differences are more than 50 deg. C. the measured temperatures cannot possibly fall so much short of the true gas temperatures. The most probable explanation is that when the kiln was stopped for the instruments to be fitted it cooled down somewhat and a true equilibrium had not yet been achieved when the gas temperature readings were taken.

The mean gas temperatures for cross-sections 10 to 12 were calculated by the same method, but allowance had to be made for the fact that in the vicinity of the flame all the heat introduced into the kiln in the mixture of coal dust and air had not yet been liberated. In the following section will be shown how the mean combustion ratio was determined experimentally for the various cross-sections.

(To be continued.)

# Tables for the Conversion of Weights and Precipitates.

On this and the following pages are given a number of useful tables for the conversion of weights of various precipitates to percentages of substances required.

TABLE I.

CONVERSION OF WEIGHT OF MAGNESIUM PYROPHOSPHATE (Mg,P,O,)
IN GRAMMES INTO PERCENTAGE OF MgO IN SUBSTANCE ANALYSED.

(HALF-GRAMME SAMPLE.)

Weight of Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> (gramme).	MgO (per cent.).	Weight of Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> (gramme).	MgO (per cent.).	Weight of $Mg_2P_2O_7$ (gramme).	MgO (per cent.)
0.0050	0.36	0.0220	1.58	0.0390	2.80
0.0055	0.40	0.0225	1.62	0.0395	2.84
0.0060	0.43	0.0230	1.66	0.0400	2.88
0.0065	0.47	0.0235	1.69	0.0405	2.92
0.0070	0.21	0.0240	1.73	0.0410	2.95
0.0075	0.54	0.0245	1.76	0.0415	2.98
0.0080	0.58	0.0250	1.80	0.0420	3.02
0.0085	0.61	0.0255	1.83	0.0425	3.06
0.0090	0.65	0.0260	1.87	0.0430	3.10
0.0095	0.68	0.0265	1.91	0.0435	3.13
0.0100	0.72	0.0270	1.94	0.0440	3.17
0.0102	0.76	0.0275	1.98	0.0445	3.21
0.0110	0.79	0.0280	2.01	0.0450	3.25
0.0115	0.83	0.0285	2.05	0.0455	3.29
0.0120	0.87	0.0290	2.08	0.0460	3.33
0.0125	0.90	0.0295	2.12	0.0465	3.37
0.0130	0.94	0.0300	2.15	0.0470	3.40
0.0135	0.97	0.0305	2.19	0.0475	3.44
0.0140	1.01	0.0310	2.23	0.0480	3.47
0.0145	1.04	0.0315	. 2.26	0.0485	3.51
0.0150	τ.08	0.0320	2.30	0.0490	3.55
0.0155	1.12	0.0325	2.33	0.0495	3.58
0.0160	1.15	0.0330	2.37	0.0500	3.62
0.0165	1.19	0.0335	2.40	0.0505	3.66
0.0170	1.23	0.0340	2.44	0.0510	3.69
0.0175	1.20	0.0345	2.48	0.0515	3.73
0.0180	1.30	0.0350	2.52	0.0520	3.77
0.0185	1.33	0.0355	2.55	0.0525	3.81
0.0100	1.37	0.0360	2.59	0.0530	3.84
0.0195	1.41	0.0365	2.62	0.0535	3.88
0.0200	1.45	0.0370	2.66	0.0540	3.92
0-0205	1.48	0.0375	2.70	0.0545	3.95
0.0310	1.51	0-0380	2.74	0.0550	3.99
0.0215	1.55	0.0385	2.76		

TABLE II.

CONVERSION OF WEIGHT OF BARIUM SULPHATE (BaSO<sub>4</sub>) INTO (1) PERCENTAGE OF S, (2) PERCENTAGE OF SO<sub>3</sub>, (3) PERCENTAGE OF CaSO<sub>4</sub>·2H<sub>2</sub>O, IN THE SUBSTANCE ANALYSED.

(ONE-GRAMME SAMPLE.)

Weight of BaSO <sub>4</sub> (gramme).	S (per cent.).	SO <sub>3</sub> (per cent.).	CaSO <sub>4</sub> .2H <sub>2</sub> O (per cent.).	Weight of BaSO <sub>4</sub> (gramme).	S (per cent.).	SO <sub>3</sub> (per cent.).	CaSO <sub>4</sub> .2H <sub>2</sub> ( (per cent.).
0.002	0.03	0.07	0.15	0.041	0.56	1.41	3.02
0.003	0.04	0.10	0.22	0.042	0.58	1.44	3.10
0.004	0.06	0.14	0.30	0.043	0.59	1.48	3.17
0.005	0.07	0.17	0.37	0.044	0.61	1.51	3.25
0.006	0.08	0.21	0.44	0.045	0.62	1.54	3.32
0.007	0.10	0.24	0.51	0.046	0.63	1.58	3.40
0.008	0.11	0.27	0.59	0.047	0.65	1.61	3.47
0.000	0.12	0.31	0.66	0.048	0.66	1.65	3.55
0.010	0.14	0.34	0.73	0.049	0.67	1.68	3.62
0.011	0.15	0.38	0.81	0.050	0.69	1.72	3.70
0.012	0.17	0.41	0.88	0.051	0.70	1.75	3.77
0.013	0.18	0.45	0.96	0.052	0.71	1.78	3.84
0.014	0.19	0.48	1.03	0.053	0.73	1.82	3.92
0.015	0.21	0.52	1.11	0.054	0.74	1.85	3.90
0.016	0.22	0.55	1.18	0.055	0.76	1.89	4.07
0.017	0.23	0.58	1.26	0.056	0.77	1.92	4.14
0.018	0.25	0.62	1.33	0.057	0.78	1.96	4.22
0.019	0.26	0.65	1.41	0.058	0.80	1.99	4.29
0.020	0.28	0.69	1.48	0.059	0.81	2.02	4.36
0.021	0.29	0.72	1.55	0.060	0.82	2.06	4.43
0.022	0.30	0.76	1.63	0.061	0.84	2.09	4:50
0.023	0.32	0.79	1.70	0.062	0.85	2.13	4.58
0.024	0.33	0.82	1.77	0.063	0.87	2.16	4.65
0.025	0.34	0.86	1.85	0.064	0.88	2.20	4.73
0.026	0.36	0.89	1.92	0.065	0.89	2.23	4.80
0.027	0.37	0.93	1.99	0.066	0.91	2.26	4.87
0.028	0.39	0.96	2.07	0.067	0.92	2.30	4.94
0.029	0.40	1.00	2.14	0.068	0.93	2.33	5.02
0.030	0.41	1.03	2.21	0.060	0.95	2.37	5.09
0.031	0.43	1.06	2.29	0.070	0.96	2.40	5.16
0.032	0.44	1.10	2.36	0.071	0.98	2.44	5.24
0.033	0.45	1.13	2.43	0.072	0.99	2.47	5.31
0.034	0.47	1.17	2.51	0.073	1.00	2.50	5.38
0.035	0.48	1.20	2.58	0.074	1.02	2.53	5.46
0.036	0.50	1.24	2.65	0.075	1.03	2.57	5.53
0.037	0.51	1.27	2.73	0.076	1.04	2.61	5.60
0.038	0.52	1.30	2.80	0.077	1.06	2.64	5.68
0.039	0.54	1.34	2.87	0.078	1.07	2.68	5.75
0.040	0.55	1.37	2.95	0.079	1.00	2.71	5.82
-		-	-	0.080	1.10	2.74	5.89

#### TABLE III.

(ONVERSION OF WEIGHT OF CALCIUM SULPHATE (CaSO,) OR CALCIUM CARBONATE (CaCO3) IN GRAMMES INTO PERCENTAGE OF CALCIUM OXIDE (CaO) IN SUBSTANCE ANALYSED.

(HALF-GRAMME SAMPLE.)

Weight of CaSO <sub>4</sub> (gramme).	Weight of CaCO <sub>3</sub> (gramme).	CaO (per cent.).	Weight of CaSO <sub>4</sub> (gramme).	Weight of CaCO <sub>3</sub> (gramme).	(per cent.)
0.729	0.536	60.03	0.781	0.574	64.32
0.731	0.538	60.20	0.783	0.576	64.48
0.733	0.539	60.36	0.785	0.577	64.65
0.735	0.541	60.53	0.787	0.579	64.81
0.737	0.542	60.69	0.789	0.580	64.98
0.739	0.544	60.86	0.791	0.582	65.14
0.741	0.545	61.02	0.793	0.583	65.31
0.743	0.546	61.19	0.795	0.585	65.47
0.745	0.548	61.35	0.797	0-586	65.64
0.747	0.549	61.52	0.799	0.588	65.80
0.749	0.551	61.68	0.801	0.589	65.96
0.751	0.552	61.85	0.803	0.591	66-13
0.753	0.554	62.01	0.805	0.592	66.29
0.755	0.555	62.18	0.807	0.594	66-46
0.757	0.557	62.34	0.809	0.595	66.62
0.759	0.558	62.51	0.811	0.597	66.78
0.761	0.560	62.67	0.813	0.598	66-95
0.763	0.561	62.84	0.815	0.599	67-11
0.765	0.563	63.00	0.817	0.601	67.28
0.767	0.564	63.17	0.810	0.602	67.44
0.769	0.566	63.33	0.821	0.604	67.61
0.771	0.567	63.50	0.823	0.605	67.77
0.773	0.569	63.66	0.825	0.607	67-94
0.775	0.570	63.83	0.827	0.608	68-11
0.777	0.571	63.99	0.829	0.610	68-27
0.779	0.573	64.15	0.831	0.611	68-44

#### TABLE IV.

CONVERSION OF WEIGHT OF MAGNESIUM PYROPHOSPHATE (Mg.P.O.) IN GRAMMES INTO PERCENTAGE OF POO, IN SUBSTANCE ANALYSED. (ONE-GRAMME SAMPLE.)

Weight of Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> (gramme).	P <sub>2</sub> O <sub>5</sub> . (per cent.).	Weight of Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> (gramme).	P <sub>2</sub> O <sub>5</sub> (per cent.).	Weight of Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> (gramme).	P <sub>2</sub> O <sub>5</sub> (per cent.)
0.0005	0.03	0.0055	0.35	0.0102	0.67
0.0010	0.06	0.0060	0.38	0.0110	0.70
0.0012	0.10	0.0065	0.42	0.0115	0.73
0.0020	0.13	0.0070	0.45	0.0120	0.77
0.0025	0.16	0.0075	0.48	0.0125	0.80
0.0030	0.10	0.0080	0.21	0.0130	0.83
0.0035	0.22	0.0085	0.54	0.0135	0.86
0.0040	0.26	0.0090	0.57	0.0140	0.80
0.0045	0.29	0.0095	0.61	0.0145	0.92
0.0050	0.32	0.0100	0.64	0.0150	0.96

TABLE V.

CONVERSION OF WEIGHT OF POTASSIUM PLATINO-CHLORIDE (K2PtCl8) IN GRAMMES INTO PERCENTAGE OF POTASSIUM CHLORIDE (KCI). (One Gramme Taken for Determination.)

Weight of K <sub>2</sub> PtCl <sub>6</sub> (gramme).	KCl (per cent.).	Weight of K <sub>2</sub> PtCl <sub>6</sub> (gramme).	KCl (per cent.).	Weight of K <sub>2</sub> PtCl <sub>6</sub> (gramme).	(per cent.)
0.001	0.03	0.040	1.22	0.079	2.41
0.002	0.06	0.041	1.25	0.080	2.44
0.003	0.09	0.042	1.28	0.081	2.48
0.004	0.12	0.043	1.31	0.082	2.51
0.005	0.15	0.044	1.34	0.083	2.54
0.006	0.18	0.045	1.38	0.084	2.57
0.007	0.21	0.046	1.41	0.085	2.60
0.008	0.24	0.047	1.44	0.086	2.63
0.009	0.28	0.048	1.47	0.087	2.66
0.010	0.31	0.049	1.50	0.088	2.69
O.OII	0.34	0.050	1.53	0.089	2.72
0.012	0.37	0.051	1.56	0.090	2.75
0.013	0.40	0.052	1.59	0.091	2.78
0.014	0.43	0.053	1.62	0.092	2.81
0.015	0.46	0.054	1.65	0.093	2.84
0.016	0.49	0.055	1.68	0.094	2.87
0.017	0.52	0.056	1.71	0.095	2.90
0.018	0.55	0.057	1.74	0.096	2.93
0.019	0.58	0.058	1.77	0.097	2.96
0.020	0.61	0.059	1.80	0.098	2.99
0.021	0.64	0.060	1.83	0.099	3.02
0.022	0.67	0.061	1.86	0.100	3.06
0.023	0.70	0.062	1.89	0.101	3.09
0.024	0.73	0.063	1.93	0.103	3.12
0.025	0.76	0.064	1.96	0.103	3.15
0.026	0.79	0.065	1.99	0.104	3.18
0.027	0.83	0.066	2.02	0.105	3.21
0.028	0.86	0.067	2.05	0.100	3.24
0.029	. 0.89	0.068	2.08	0.107	3.27
0.030	0.92	0.069	2.11	e 0.108	3.30
0.031	0.95	0.070	2.14	0.109	3.33
0.032	<b>.</b> 0.98	0.071	2.17	0.110	3.36
0.033	1.01	0.072	2.20	0.111	3.39
0.034	1.04	0.073	2.23	0.112	3.42
0.035	1.07	0.074	2.26	0.113	3.45
0.036	1.10	0.075	2.29	0.114	3.48
0.037	1.13	0.076	2.32	0.115	3.51
0.038	1.16	0.077	2.35	0.119	3.54
0.039	1.19	0.078	2.38	0.117	3.57
-	_			0.118	3.61

TABLE VI.

CONVERSION OF WEIGHT OF POTASSIUM PLATINO-CHLORIDE (K2PtCl4) INTO PERCENTAGE OF POTASSIUM OXIDE (K2O). (ONE GRAMME TAKEN FOR DETERMINATION.)

Weight of K <sub>2</sub> PtCl <sub>6</sub> (gramme).	K <sub>2</sub> O (per cent.).	Weight of K <sub>2</sub> PtCl <sub>6</sub> (gramme).	K <sub>2</sub> O (per cent.).	Weight of K <sub>2</sub> PtCl <sub>6</sub> (gramme).	K <sub>2</sub> O (per cent.)
0.001	0.02	0.053	1.02	0.105	2.03
0.003	0.06	0.055	1.06	0.107	2.07
0.005	0.10	0.057	1.10 4	0.100	2.10
0.007	0.14	0.059	1.14	0.111	2-14
0.009	0.17	0.061	1.18	0.113	2.18
0.011	0.21	0.063	1.22	0.115	2.22
0.013	0.25	0.065	1.26	0.117	2.26
0.015	0.29	0.067	1.29	0.119	2.30
0.017	0.33	0.069	1.33	0.121	2.34
0.019	0.37	0.071	1.37	0.123	2.37
0.021	0.41	0.073	1.41	0.125	2.41
0.023	0.44	0.075	1.45	0.127	2.45
0.025	0.48	0.077	1.49	0.129	2.49
0.027	0.52	0.079	1.53	0.131	2.53
0.029	0.56	0.081	1.56	0.133	2.57
0.031	0.60	0.083	1.60	0.135	2.61
0.033	0.64	0.085	1.64	0.137	2.64
0.035	0.68	0.087	1.68	0.139	2.68
0.037	0.71	0.089	1.72	0.141	. 2.72
0.039	0.75	0.091	1.76	0-143	2.76
0.041	0.79	0.093	1.80	0.145	2.80
0.043	0.83	0.095	1.83	0.147	2.84
0.045	0.87	0.097	1.87	0.149	2.88
0.047	0.91	0.099	1.91	0.151	2.91
0.049	0.95	0.101	1.95	0.153	2.95
0.051	0.98	0.103	1.99		

TABLE VII.

CONVERSION OF WEIGHT OF SODIUM CHI.ORIDE (Nacl) INTO PERCENTAGE OF SODIUM OXIDE (Na $_2$ O).

(ONE GRAMME TAKEN FOR DETERMINATION.)

Weight of NaCl (gramme).	Na <sub>2</sub> O (per cent.).	Weight of NaCl (gramme).	Na <sub>2</sub> O (per cent.).	Weight of NaCl (gramme).	Na <sub>2</sub> O (per cent.)
0.001	0.05	0.020	1.06	0.039	2.07
0.002	0.11	0.021	1.11	0.040	2.12
0.003	0.16	0.022	1.17	0.041	2-17
0.004	0.21	0.023	1.22	0.042	2.23
0.005	0.27	0.024	1.27	0.043	2.28
0.006	0.32	0.025	1.33	0.044	2.33
0.007	0.37	0.026	1.38	0.045	2.39
0.008	0.42	0.027	1.43	0.046	2.44
0.009	0.48	0.028	1.49	0.047	2.49
0.010	0.53	0.029	1.54	0.048	2.55
0.011	0.58	0.030	1.59	0.049	2.60
0.012	0.64	0.031	1.64	0.050	2.65
0.013	0.69	0.032	1.70	0.051	2.71
0.014	0.74	0.033	1.75	0.052	2.76
0.015	0.80	0.034	1.80	0.053	2.81
0.016	0.85	0.035	1.86	0.054	2.86
0.017	0.90	0.036	1.91	0.055	2.91
0.018	0.96	0.037	1.96	0.056	2.97
0.019	1.01	0.038	2.02	0.057	3.02

## London County Council Building By-laws Relating to Concrete Work.

SPECIFICATION FOR HIGH-ALUMINA CEMENT.

New London County Council building by-laws, made under the London Building Act (Amendment) Act, 1935, came into force on January 1 last. So far as concrete and reinforced concrete design are concerned, the new by-laws largely follow the Recommendations for a Code of Practice for the use of Reinforced Concrete in Building, issued by the Building Research Station in 1934, although these recommendations have not been adopted entirely.

The by-laws relating to cement are as follows, and it will be noted that they include, we believe for the first time in this country, a specification for aluminous cement.

"12. Cement shall be Portland cement, Portland blastfurnace cement, or high-alumina cement, but no two of such cements shall be used in combination.

"Portland cement shall comply with the British Standard Specification for Portland Cement number 12—1931.

"Portland blastfurnace cement shall comply with the British Standard Specification for Portland Blastfurnace Cement number 146—1932.

"High-alumina cement shall consist of aluminous and calcareous materials which have been fused to a molten state and ground to such a degree of fineness that the cement will not leave a residue of more than 12 per cent. by weight on a No. 170 mesh and not more than I per cent. on a No. 72 mesh. The cement shall contain not less than 35 per cent. by weight of alumina, and the ratio of percentage by weight of alumina to that of lime shall be not less than o.g. When gauged with 22 per cent. by weight of water it shall not begin to set before the expiration of two hours but shall begin to set within 6 hours of gauging and the final setting shall take place within 2 hours of the initial setting. The strength of high-alumina cement shall be such that when a mortar is composed of one part by weight of high-alumina cement to three parts by weight of white Leighton Buzzard sand graded to pass a No. 18 mesh and stop on a No. 25 mesh, and the whole is gauged with a weight of water equal to 8 per cent. of the dry materials, such mortar shall have a tensile strength of not less than 475 lb. per square inch within 24 hours after gauging and within seven days its tensile strength shall have increased and shall be not less than 550 lb. per square inch.

"Wherever cement is used it shall not be moved or disturbed after one hour from the time it has come into contact with water until it has set hard."

In Clause 14 it is stipulated that the quantity of water for making highalumina cement concrete shall be sufficient, but not more than sufficient, to produce a sound concrete, and the concrete must be kept wet for 24 hours after gauging.

#### Method of Making and Testing Cubes.

Standard methods of making cube tests of concrete are included in the by-laws. These are as follows:

Standard Method of Making Preliminary Cube Tests of Concrete.—The method described applies to compression tests of concrete made in a laboratory where accurate control of materials and test conditions is possible.

MATERIALS AND PROPORTIONING.—The materials and the proportions used in making the preliminary tests shall be similar in all respects to those to be employed in the work. The water content shall be as nearly as practicable equal to that to be used in the work, but shall be not less than the sum of 30 per cent. by weight of the cement and 5 per cent. by weight of the aggregate unless specially authorised by the district surveyor. For porous aggregates additional water shall be used to allow for the amount absorbed by the aggregates.

Materials shall be brought to room temperature (58 deg. to 64 deg. F.) before beginning the tests. The cement on arrival at the laboratory shall be mixed dry either by hand or in a suitable mixer in such a manner as to ensure as uniform a material as possible, care being taken to avoid intrusion of foreign matter. The cement shall then be stored in air-tight containers until required. Aggregates shall be in a dry condition when used in concrete tests.

The quantities of cement, aggregate and water for each batch shall be determined by weight to an accuracy of 1 part in 1,000.

MIXING CONCRETE.—The concrete shall be mixed by hand or in a small batch mixer in such a manner as to avoid loss of water. The cement and fine aggregate shall first be mixed dry until the mixture is uniform in colour. The coarse aggregate shall then be added and mixed with the cement and sand. The water shall then be added and the whole mixed thoroughly for a period of not less than two minutes and until the resulting concrete is uniform in appearance.

Consistency.—The consistency of each batch of concrete shall be measured, immediately after mixing, by the slump test. Provided that care is taken to ensure that no water is lost the material used for the slump tests may be re-mixed with the remainder of the mix before making the test specimen.

Size of Test Cubes.—Compression tests of concrete shall be made on 6-in. cubes. The mould shall be of metal with inner faces accurately machined in order that the opposite sides of the specimen shall be plane and parallel. Each mould shall be provided with a metal base, having a smooth machined surface. The interior surfaces of the mould and base shall be slightly oiled before concrete is placed in the mould.

COMPACTING.—Concrete test cubes shall be moulded by placing the fresh concrete in the mould in three layers, each layer being rammed with a steel bar 15 in. long and having a ramming face of 1 in. square and a weight of 4 lb. For mixes of 1½ in. slump or less, 35 strokes of the bar shall be given for each layer; for mixes of wetter consistency the number may be reduced to 25 strokes per layer.

CURING.—All test cubes shall be placed in moist air of at least 90 per cent. relative humidity and at a temperature of 58 deg. F. to 64 deg. F. for 24 hours ( $\pm \frac{1}{2}$  hour) commencing immediately after moulding is completed. After 24 hours the test cubes shall be marked, removed from the moulds, and placed in water at a temperature of 58 deg. F. to 64 deg. F. until required for test.

METHOD OF TESTING.—All compression tests on concrete cubes shall be made between smooth plane steel plates, without end packing, the rate of loading being kept approximately at 2,000 lb. per square inch per minute. One compression plate of the machine shall be provided with a ball seating in the form of a portion of a sphere, the centre of which falls at the central point of the face of the plate.

All test cubes shall be placed in the machine in such a manner that the load shall be applied to the sides of the cubes as cast.

DISTRIBUTION OF SPECIMENS AND STANDARD OF ACCEPTANCE.—For each age at which tests are required, three cubes shall be made and each of these shall be taken from a different batch of concrete.

The acceptance limits are a difference of 15 per cent. of the average strength between the maximum and minimum recorded strengths of the three cubes. In cases where this is exceeded repeat tests shall be made, excepting where the minimum strength test result does not fall below the strength specified.

Standard Method of Making Works Cube Tests of Concrete.—The method described applies to compression tests of concrete sampled during the progress of the work.

Size of Test Cubes and Moulds.—The test specimens shall be 6-in. cubes. The moulds shall be of metal, with inner faces accurately machined in order that opposite sides of the specimen shall be plane and parallel. Each mould shall be provided with a metal base plate, having a smooth machined surface. The interior surfaces of the mould and base shall be slightly oiled before concrete is placed in the mould.

SAMPLING.—Wherever practicable concrete for the test cubes shall be taken immediately after it has been deposited in the work. Where this is impracticable samples shall be taken as the concrete is being delivered at the point of deposit, care being taken to obtain a representative sample. All the concrete for each sample shall be taken from one place. A sufficient number of samples, each large enough to make one test cube, shall be taken at different points so that the test cubes made from them will be representative of the concrete placed in that portion of the structure selected for tests. The location from which each sample is taken shall be noted clearly for future reference.

In securing samples the concrete shall be taken from the mass by a shovel or similar implement and placed in a large clean pail or other receptacle for transporting to the place of moulding. Care shall be taken to see that each test cube represents the total mixture of concrete from a given place. Different samples shall not be mixed together, but each sample shall make one cube. The receptacle containing the concrete shall be taken to the place where the

cube is to be moulded as quickly as possible and the concrete shall be slightly re-mixed before placing in the mould.

Consistency.—The consistency of each sample of concrete shall be measured, immediately after re-mixing, by the slump test.

Providing that care is taken to ensure that no water is lost, the material used for the slump tests may be re-mixed with the remainder of the mix before making the test cube.

Compacting.—Concrete test cubes shall be moulded by placing the fresh concrete in the mould in three layers, each layer being rammed with a steel bar 15 in. long and having a ramming face of 1 in. square and a weight of 4 lb. For mixes of  $1\frac{1}{2}$  in. slump or less, 35 strokes of the bar shall be given for each layer; for mixes of wetter consistency the number may be reduced to 25 strokes per layer.

Curing.—The test cubes shall be stored at the site of construction at a place free from vibration, under damp sacks for 24 hours ( $\pm \ _2$  hour), after which time they shall be removed from their moulds, marked and buried in damp sand until the time for sending to the testing laboratory. They shall then be well packed in damp sand or other suitable damp material and sent to the testing laboratory, where they shall be similarly stored until the date of test. Test cubes shall be kept on the site for as long as practicable and for at least three-fourths of the period before test, except for tests at ages less than seven days. The temperature of the place of storage on the site shall not be allowed to fall below 40 deg. F., nor shall the cubes themselves be artificially heated.

RECORD OF TEMPERATURES.—A record of the maximum and minimum day and night temperatures at the place of storage of the cubes shall be kept during the period the cubes remain on the site.

METHOD OF TESTING.—All compression tests on concrete cubes shall be made between smooth plane steel plates without end packing, the rate of loading being kept approximately at 2,000 lb. per square inch per minute. One compression plate of the machine shall be provided with a ball seating in the form of a portion of a sphere, the centre of which falls at the central point of the face of the plate.

All test cubes shall be placed in the machine in such a manner that the load shall be applied to the sides of the cubes as cast.

#### Design and Operation of Modern Lime Works.

The series of articles by Dr. W. V. S. Knibbs, D.Sc., on "Design and Operation of Modern Lime Works," will be continued in our next issue.

#### The Constituents of Clinker.

H. E. Schwiete gives in *Tonindustrie Zeitung* (Nos. 28-31, 1937), a review of the present position of research on cement clinker, commencing with the chemistry of Portland cement consisting chiefly of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and CaO with small amounts of MgO and alkalis which influence the sintering process. The following is an abstract of the paper:

The basis of the investigation of the constitution of Portland cement consists of physico-chemical equilibria in the quaternary system  $CaO-Al_2O_3-SiO_2-Fe_2O_3$  and the ternary system  $CaO-Al_2O_3-SiO_2$ . The theoretical order of crystallisation in a mixture of  $CaO-Al_2O_3-SiO_2$  with the composition of Portland cement is described, and it is shown that the following compounds are formed: CaO,  $CaO-SiO_2$  (CaS), and  $CaO-Al_2O_3$  ( $CaO-Al_2O_3$  (CaS) in lime-rich mixes;  $CaS-Al_2O_3$  ( $CaS-Al_2O_3$ ) and  $CaS-Al_2O_3$  in low lime mixes.

In practice there are three different stages of clinker formation, namely, heating, sintering, and cooling. During heating, first the  $\mathrm{CO_2}$  present in the raw material is driven off, then the oxides react in the solid state: lime and silica form  $\mathrm{C_2S}$ , lime and alumina form aluminates. Since in commercial manufacture the time of heating is very short, the theoretical conversion of  $\mathrm{CaO}$  and  $\mathrm{C_2S}$  to  $\mathrm{C_3S}$  is incomplete. Complete combination occurs during sintering. If the raw material is fine enough the short time of burning at the sintering temperature is sufficient for all the lime to combine and for an equilibrium to be reached in which  $\mathrm{C_3S}$ ,  $\mathrm{C_2S}$ , and  $\mathrm{C_3A}$  are produced. In the last stage the equilibrium is frozen due to rapid cooling and resorption cannot occur, so that the flux forms a glass or crystallises independently. With additions of  $\mathrm{Fe_2O_3}$  the compound  $\mathrm{4CaO}$ .  $\mathrm{Al_2O_3}$ - $\mathrm{Fe_2O_3}$  ( $\mathrm{C_4AF}$ ) can form and the melting point of the flux is reduced by about 120 deg.  $\mathrm{C}$ .

The compounds which may form in clinker are then described. These are principally alite  $(C_2S)$ , belite  $(C_2S)$ , and celite (ground mass).

The methods of research are described, especially the optical methods. It is pointed out that these can be carried out by transmitted or reflected light if powdered specimens or thin sections about  $20\mu$  thick are used. The examination is made with a polarising microscope and the following properties are determined: colour, crystal habit, texture, refractive index, pleochroism, birefringence, twinning, extinction angle, cleavage, optical character and optic axial angle. Several photomicrographs of thin sections of cement clinker showing the chief compounds are reproduced, and the properties of the various constituents tabulated with detailed descriptions.

The quantitative determination of the clinker components is carried out on thin sections under the microscope. The errors in this method are about  $\pm$  2 per cent. for good sections and about  $\pm$  5 per cent, when the components are not well crystallised. The results from measurements with the micrometer ocular on two clinker sections from each of two cements are tabulated, and the author shows that good agreement can be obtained.

Examination in reflected light is then described. For this a polished specimen must be suitably etched (Tavasci's method). The advantages and disadvantages of the microscopical method are discussed, and the author points out that though a conclusion regarding the constitution can be arrived at in a comparatively short time this is based on a few pieces of clinker which must represent the whole burn. Nevertheless, the good agreement obtained among specimens from the same burn justifies the use of this method. The advantage of examination in reflected light over that in transmitted light is that the specimens are easier to prepare and, by etching, a particular type of crystal can be made prominent. The disadvantage is that natural colours are lost.

The author goes on to describe the X-ray method of investigation according to Debye and Scherrer. These tests are made on pulverised specimens and it is possible to determine the amounts of the various types of crystals by measuring the intensity of the lines characteristic of each component. The sensitivity of the method depends on the technique, and especially on the symmetry and structure of the crystal under investigation. The limit of sensitivity lies, in the case of crystals with a low order of symmetry, between 5 and 10 per cent. and, for crystals with a high order of symmetry, as low as 1 per cent. The advantage of the X-ray method over the microscopical method is that particles less than 1  $\mu$  in diameter can be detected which cannot be distinguished under the microscope. The method is illustrated with X-ray powder photographs.

A detailed discussion of the value of chemical methods of investigation follows, and the method of calculating the amounts of the constituents is given. It is important that the free lime content should be known as otherwise the results may be inaccurate. It is pointed out that the determination of the free lime content is indispensable for judging the quality of clinker.

In a diagram the author shows the limits of variation of analytical results when the analyses are made by experienced chemists. From the various analyses the constitution is calculated and the results given in a table. It is shown, for instance, that the C<sub>3</sub>S content can vary from 5.7 to 6.9.9 per cent., and the C<sub>2</sub>S content from 5.7 to 16.7 per cent. for the same cement according to the analysis taken. The method of calculation according to Bogue and corrected by Lea is also given.

The paper is accompanied by a number of tables, diagrams, photomicrographs, and an extensive bibliography.

### Burning Small Limestone.

A FIRM of lime burners on the Continent inform us that they wish to calcine small limestone (grains from 0.5 to 6 mm. in diameter) in a rotary kiln using anthracite coal with 5 per cent. of volatile material, and ask whether we have any knowledge of similar small stone being used in this country.

So far as we are aware limestone of this size is not at present calcined in rotary kilns, and the results obtained in the past with such sandy material have been poor. Theoretically there is no reason why such small material should not successfully be calcined in a rotary kiln, but, because it is seldom available commercially, the problem of its calcination has not been specifically studied. Anthracite is not used for rotary-kiln firing, but it may be used for dust firing or in a producer to make gas for gas firing. At present anthracite of the quality indicated is used for lime burning only in mixed-feed shaft kilns.

## Effect of Granulometric Composition and Various Salts on the Heat of Hydration and the Mechanical Properties of Portland Cement.

In the Journal of Applied Chemistry [(U.S.S.R.), Vol. 9, pp. 1937–50, 1936], Messrs. P. P. Budnikoff and L. G. Gulinova state that from experiments with the Budnikoff calorimeter they have come to the following conclusions:

Additions of calcium chloride, aluminium chloride, dolomite burned at 700 deg. C., and by-products from the manufacture of alumina from bauxite in amounts of I to 2 per cent., increase the strength, shorten the setting time, and raise the heat of hydration of Portland cement. These substances are recommended for use in winter to avoid the need for artificial heating when placing concrete.

Sodium fluosilicate has a comparatively small effect on the strength of Portland cement, but reduces the setting time to one-tenth of its normal value with an addition of  $2\frac{1}{2}$  per cent. This type of addition can therefore be used with high-early-strength cements for road making, etc.

Magnesium chloride in amounts of I to 2 per cent. increases strength, shortens setting time, and reduces the heat of hydration of the cement. This addition can be used in mass concrete where, by reducing the heat of hydration, it is possible to avoid internal stresses in the concrete. Barium chloride, soda, calcium hydrate, and caustic soda are not recommended as additions because they reduce the strength of the cement.

The investigation also showed that the rate of heat evolution is inversely proportional to the diameter of the cement particles.

### High-Magnesia Lime.

Mr. M. A. Teixeira de Castro, of S. Paulo, Brazil, writes as follows: "I have read in your issue for November, 1937, a reference to the possible use in England, on a commercial scale, of high-magnesia lime as visualised by the Building Research Station. In São Paulo (Brazil) a high-magnesia lime having the following chemical composition:

SiO <sub>2</sub>			2.1
Al <sub>2</sub> O <sub>3</sub>			1.0
$Fe_2O_3$			0.9
CaO			43.0
MgO	*		27.5
Loss			25.5
Total			100.0

has successfully been used for over twenty years in plastering, mortars, and other building work."